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Photocatalytic decomposition of dispiro(diadamantane-1,2-dioxetane) (1) to adamantanone (2) initiated by Ce(ClO<sub>4</sub>)<sub>3</sub> in the excited state in the MeCN--CHCl<sub>3</sub> (2 : 1) mixture was studied. The bimolecular rate constants of quenching  $k_q$  were determined from the kinetics of quenching of Ce<sup>3+\*</sup> by dioxetane at different temperatures. The Arrhenius parameters of the quenching were calculated from the temperature dependence of  $k_q$ :  $E_a = 3.2\pm0.3$  kcal mol<sup>-1</sup> and log  $A = 11.6\pm0.6$ . The quantum yields of photolysis of 1 depending on its concentration and the rate constant of the chemical reaction of Ce<sup>3+\*</sup> with 1 were determined. The latter coincides with  $k_q$ :  $k_{ch} = (2.6\pm0.3) \cdot 10^9$  L mol<sup>-1</sup>s<sup>-1</sup> (T = 298 K). The fact that the maximum quantum yield of decomposition of dioxetane is equal to 1 indicates the absence of physical quenching of Ce<sup>3+\*</sup> by dioxetane. It is believed that the electron transfer occurs in the reaction of Ce<sup>3+\*</sup> with 1. Nonradiative deactivation of Ce<sup>3+\*</sup> in solutions of MeCN and in MeCN--CHCl<sub>3</sub> mixtures was studied. It is caused by the replacement of H<sub>2</sub>O molecules in the nearest coordination surroundings of Ce<sup>3+\*</sup> by solvent molecules and reversible transfer of an electron to the ligand. The activation parameters of the nonradiative deactivation of Ce<sup>3+\*</sup> were determined.

Key words: photocatalysis, quenching, energy transfer, dioxetane, cerium perchlorate.

1,2-Dioxetanes (four-membered cyclic peroxides) decompose into carbonyl fragments under the action of UV or IR irradiation.<sup>1,2</sup> The transfer of excitation energy from a donor to the vibrational terms of dioxetane also favors its decomposition. In these systems, the sensitized decomposition of peroxide can occur with a quantum yield >1.<sup>3,4</sup> Both polyaromatic promoters<sup>5</sup> and luminescent metal complexes<sup>4,6</sup> can act as sensitizers. The decomposition of dioxetane initiated, *e.g.*, by an excited europium chelate, is caused by the formation of a complex and by the intracomplex transfer of energy from Eu<sup>111\*</sup> to dioxetane (Scheme 1). The energy released in the decomposition of dioxetane results in the regeneration of excited Eu<sup>111\*</sup> and its further participation in the photocatalytic process.

Dioxetane also decomposes due to reversible electron transfer, for example, when a  $Ru^{II}$  trisdipyridyl complex is irradiated in solution (Scheme 2).<sup>6</sup>

Photocatalysis by lanthanides via Scheme 2 is the most probable using  $Ce^{3+}$ , since this ion has the lowest oxidation potential of the lanthanides. The photochemical activity of cerium in the reaction with dioxetane has been previously demonstrated<sup>7</sup> using  $CeCl_3$  as an example.



Scheme 2



In the present work, the photodecomposition of dispiro(diadamantane-1,2-dioxetane) (1) to adamantanone (2) initiated by excited cerium perchlorate (Scheme 3) was studied.

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# Experimental

Cerium(III) perchlorate (chemical purity grade) was purified by recrystallization and dried *in vacuo* until the Ce(ClO<sub>4</sub>)<sub>3</sub> · 4H<sub>2</sub>O composition was achieved. Acetonitrile (special purity grade) and a MeCN-CHCl<sub>3</sub> (2 : 1) mixture were used as solvents. Chloroform was purified by distillation.

Absorption spectra were recorded on a Specord M-40 spectrophotometer. Photoluminescence spectra were recorded on an MPF-4 Hitachi spectrofluorimeter. Quantum yields of photoluminescence of Ce(ClO<sub>4</sub>)<sub>3</sub> in MeCN and MeCN— CHCl<sub>3</sub> were determined by a cerium standard.<sup>8</sup> The lifetime of Ce<sup>3+</sup> in the excited state was measured on a LIF-200 laser pulse fluorimeter. Samples were irradiated in the cell chamber of the fluorimeter by light with  $\lambda = 285\pm10$  nm that was separated from the emission spectrum of a xenon lamp using a monochromator. The intensity of the light flux was determined by a ferrioxalate actinometer.<sup>9</sup> The volume of the solution irradiated was 2 mL, and the intensity of the light flux  $l = 9.5 \cdot 10^{13}$  photon s<sup>-1</sup>.

The concentration of 1 during photolysis was studied by the chemiluminescence method. The basis of the method is determination of the intensity of chemiluminescence  $(I_{CL})$ under isothermal conditions. The intensity is proportional to the concentration of 1. At the initial moment and at specified intervals (1.5-2 h), an aliquot of the photolyzed solution (0.02 mL) was taken and placed in a cell containing MeCN (2 mL). Then the intensity of luminescence was monitored at constant temperature (80 °C). The time dependence of  $I_{CL}$ corresponded to the kinetics of consumption of 1 during photolysis. The viscosity of the MeCN--CHCl<sub>3</sub> mixture ( $\eta$ ) was determined using a capillary viscosimeter.

# **Results and Discussion**

Quenching of luminescence of  $Ce(ClO_4)_3$  by dioxetane 1 in MeCN and MeCN-CHCl<sub>3</sub>. The absorption, excitation, and luminescence spectra of Ce<sup>3+</sup> perchlorate in MeCN are presented in Fig. 1. As can be seen in Fig. 1, the absorption spectrum consists of several diffuse bands at  $\lambda_{max} = 222$ , 235, and 265 nm and an inflection at 252 nm. According to the published data,<sup>8</sup> this corresponds to the parity-allowed dipole-dipole transitions from the lower sublevel  ${}^{2}F_{5/2}$  of the split term  ${}^{2}F$  of the [Xe] 5s<sup>2</sup>5p<sup>6</sup>5d configuration of the solvated Ce<sup>3+</sup> ion. It is noteworthy that the absorption spectra are very sensitive to the solvate surroundings of the Ce<sup>3+</sup> ions. For example, the absorption spectrum of Ce3+ in water consists of six bands in the  $\lambda = 200-300$  nm region (see Refs. 10 and 11), whose positions differ from those of the bands of  $Ce(CIO_4)_3$  in MeCN and in the MeCN-



Fig. 1. Absorption (1), excitation (2-4), and luminescence (5-7) spectra of Ce(ClO<sub>4</sub>)<sub>3</sub> in MeCN-CHCl<sub>3</sub> (2 : 1, v/v) at 295 K. 1, [Ce<sup>3+</sup>] =  $5 \cdot 10^{-3} \text{ mol } L^{-1}$ , [1] =  $5 \cdot 10^{-3} \text{ mol } L^{-1}$ ; 2 and 5, [Ce<sup>3+</sup>] =  $5 \cdot 10^{-3} \text{ mol } L^{-1}$ , in the absence of 1; 3 and 6, [Ce<sup>3+</sup>] =  $5 \cdot 10^{-3} \text{ mol } L^{-1}$ , [1] =  $3 \cdot 10^{-3} \text{ mol } L^{-1}$ ; 4 and 7, [Ce<sup>3+</sup>] =  $5 \cdot 10^{-3} \text{ mol } L^{-1}$ , [1] =  $5 \cdot 10^{-3} \text{ mol } L^{-1}$ ; For 2-4:  $\lambda_{\rm rm} = 384 \text{ nm}$ ,  $\Delta \lambda = 2 \text{ nm}$ . For 5-7:  $\lambda_{\rm exc} = 384 \text{ nm}$ ,  $\Delta \lambda = 2 \text{ nm}$ .

CHCl<sub>3</sub> mixture. This is associated with the existence of several forms of the solvated cerium ion. In aqueous solutions, the main absorbing form is an outer-sphere complex of Ce<sup>3+</sup> with an anion, and water is present in the inner coordination sphere.<sup>11</sup> In acetonitrile solutions, acetonitrile is likely within the coordination sphere, which results in changes in the absorption spectra. The luminescence spectrum (see Fig. 1) corresponds to the  ${}^{2}D(5d) \rightarrow {}^{2}F_{5/2}(4f)$  and  ${}^{2}D(5d) \rightarrow {}^{2}F_{7/2}(4f)$  transitions of Ce<sup>3+</sup> and is a diffuse band at  $\lambda_{max} = 390$  nm and a halfwidth  $\Delta \lambda = 66$  nm. The luminescence spectrum weakly overlaps the absorption spectrum, and the Stokes shift is equal to  $1.2 \cdot 10^4$  cm<sup>-1</sup>.

The effect of additives of 1 on the excitation and luminescence spectra (see Fig. 1) indicates that the electronic structure of Ce3+ changes after excitation. This is likely associated with the arrangement of the surroundings of the rare-earth ion, i.e., the absorbing and luminescent forms of Ce3+ in acetonitrile solutions differ. In addition, in both the luminescence and excitation spectra, redistribution of the intensity occurs as the concentration of 1 increases. This indicates that Ce3+\* reacts with 1, although, most likely, the complex is formed in the ground state as well. The most probable mechanism of this rearrangement is insertion of the anion and 1 into the first coordination sphere of the excited Ce3+ ion to form a luminescent exciplex via Scheme 4 in which S is the solvent molecule and A is the perchlorate anion.

# $[Ce^{3+*} \cdot nS] \cdot 1 \cdot A \longrightarrow [Ce^{3+*} \cdot nS] \cdot 1 \cdot A + (n - m)S$ $\downarrow hv_{abs} \qquad \qquad \downarrow hv_{lum}$ $[Ce^{3+*} \cdot nS] \cdot 1 \cdot A \longrightarrow [Ce^{3+*} \cdot nS] \cdot 1 \cdot A + (n - m)S$

Scheme 4

It is likely that the rearrangement of the surroundings of  $Ce^{3+}$  occurs due to a sharp change in the properties and sizes of the electronic cloud of the rareearth ion when an electron is transferred from the shielded 4f-shell to the terms of the [Xe]  $5s^25p^66d$ configuration.

The luminescence spectra of  $Ce^{3+}$  in MeCN-CHCl<sub>3</sub> at different temperatures are presented in Fig. 2. The shift of the luminescence maximum with temperature is not greater than 6 cm<sup>-1</sup> deg<sup>-1</sup>, and the change in the half-width is equal to 2 cm<sup>-1</sup> deg<sup>-1</sup>. As can be seen, the intensity of luminescence of  $Ce^{3+}$  decreases as the temperature increases.

The following equation can be written for the fluorescence intensity  $(I_{FL})$ :

$$I_{\rm FL} = \phi k_{\rm id} [{\rm Ce}^{3+\bullet}], \tag{1}$$

where  $\phi$  is the quantum yield of luminescence;  $k_{id}$  is the rate constant of the radiative deactivation of the Ce<sup>3+\*</sup> ion.

In aqueous solutions,  $Ce(ClO_4)_3$  luminesces with  $\phi = 1$ . This suggest that nonradiative deactivation of the



Fig. 2. Luminescence spectra for  $[Ce^{3+}] = 10^{-2} \text{ mol } L^{-1}$ : at 295 (1), 315 (2), 318 (3), 323 (4), 327 (5), and 330 (6) K  $(\lambda_{exc} = 285 \text{ nm}, \Delta \lambda = 1 \text{ nm})$ 

excited <sup>2</sup>D(5d)-state of Ce<sub>aq</sub><sup>3+</sup> is absent, and the quantum yield of luminescence and lifetime of Ce<sup>3+\*</sup>  $\tau_{id}$  = 44 ns are temperature-independent in the range from 10 to 80 °C (see Ref. 11). In MeCN and in the MeCN--CHCl<sub>3</sub> mixture,  $\phi < 1$  and depends on the temperature (Table 1). This indicates that a nonradiative channel of degradation of the excitation energy appears in the process of the deactivation of Ce<sup>3+\*</sup> in these solutions. When the intensity of the exciting light is constant the quantum yield of luminescence can be determined as the ratio of the radiative constant of the deactivation rate to the sum of the rate constants of radiative and nonradiative ( $k_d$ ) deactivation:

$$\phi = \frac{k_{\rm id}}{k_{\rm id} + k_{\rm d}},\tag{2}$$

where  $k_{id} = 1/\tau_{id} = 2.3 \cdot 10^7 \text{ L mol}^{-1} \text{ s}^{-1}$ .

The temperature change in  $\phi$  (Tables 1 and 2) is likely caused by the change in  $k_d$ . We obtain from Eq. (2) that

$$k_{\rm d} = k_{\rm id} \frac{1 - \phi}{\phi} \,. \tag{3}$$

The  $k_d$  values calculated from Eq. (3) for solutions in MeCN and MeCN-CHCl<sub>3</sub> are presented in Tables 1

**Table 1.** Emission yields  $\phi$  and rate constants of nonradiative deactivation  $k_d$  of Ce<sup>+</sup>(ClO<sub>4</sub>)<sub>3</sub> in MeCN at different temperatures

T/K	φ	k <sub>d</sub> · 10 <sup>-6</sup> /s <sup>-1</sup>	
295	0.78	6.5	
308	0.66	11.8	
315	0.59	16.0	
318	0.54	19.6	
323	0.51	22.1	
326	0.46	27.0	
330	0.40	34.5	
341	0.30	53.7	
345	0.25	69.0	

Note. The values of emission yields were determined with an error of  $\pm 5\%$ .

**Table 2.** Emission yields  $\phi$ , rate constants of nonradiative deactivation  $k_d$ , and lifetimes of Ce<sup>\*</sup>(ClO<sub>4</sub>)<sub>3</sub> in MeCN-CHCl<sub>3</sub>; Stern constants  $K_s$  and bimolecular constants  $k_q$  for quenching Ce<sup>\*</sup>(ClO<sub>4</sub>)<sub>3</sub> by dioxetane 1 at different temperatures

T/K	¢	$k_{\rm d} \cdot 10^{-7}$ /s <sup>-1</sup>	<i>K</i> s /L mol <sup>-1</sup>	τ <sub>0</sub> /ns	$k_{q} \cdot 10^{-9}$ /L mol <sup>-1</sup> s <sup>-1</sup>	-
295	0.66	1.20	59	28	2.1	-
315	0.60	1.53	58	25	2.3	
318	0.52	2.12	56	22	2.6	
322	0.43	3.04	53	18	3.0	
331	0.34	4.46	52	14	3.7	
335	0.30	5.37	50	13	3.8	

Note. The values of emission yields were determined with an error of  $\pm 5\%$ , the values of  $K_S$ ,  $\tau_0$ , and  $k_q$  were calculated with an error of  $\pm 3\%$ .

and 2. It was determined from the temperature dependence in the Arrhenius coordinates that  $E_a = 9.5 \pm$ 0.4 kcal mol<sup>-1</sup> and logA =  $13.8\pm0.5$  for solutions in MeCN and  $E_a = 7.5\pm0.6$  kcal mol<sup>-1</sup> and logA =  $12.6\pm0.7$ for the MeCN-CHCl3 mixture. The significant differences in  $E_a$  suggest that the dynamics of the interaction between the solvent molecules changes as the temperature increases. Since a hydrated salt was used for preparing the solutions, H<sub>2</sub>O molecules were certainly present in the coordination sphere along with the solvent molecules. Perhaps, in MeCN and MeCN-CHCl3 the temperature dependences of  $\phi$  and, hence, of  $k_d$  are associated with the replacement of H<sub>2</sub>O by MeCN and CHCl<sub>3</sub> in the coordination sphere and the nonradiative transfer of energy to the vibrational terms of the solvent molecules or with electron phototransfer followed by fast recharging:

$$Ce^{3+*} + MeCN \longrightarrow [Ce^{3+*} \cdot MeCN] \longrightarrow [Ce^{4+} \cdot MeCN^{-*}] \longrightarrow [Ce^{3+} + MeCN], (4)$$

These processes are typical of quenching of Ce<sup>3+\*</sup> <sup>12</sup>

The addition of dioxetane 1 results in a general decrease in the intensity of luminescence of  $Ce^{3+}$ 



Fig. 3. Temperature dependence of the intensity of luminescence of Ce(ClO<sub>4</sub>)<sub>3</sub> in MeCN (1) and in MeCN-CHCl<sub>3</sub> (2-7) in the presence of dioxetane 1: 0 (2),  $0.742 \cdot 10^{-2}$  (3),  $1.48 \cdot 10^{-2}$  (4),  $2.97 \cdot 10^{-2}$  (5),  $4.45 \cdot 10^{-2}$  (6), and  $6.67 \cdot 10^{-2}$  (7) mol L<sup>-1</sup>.

(Fig. 3). The kinetics of quenching of  $Ce^{3+*}$  by dioxetane in Stern-Volmer coordinates is presented in Fig. 4:

$$I_0/I = 1 + K_{\rm S}[1], \tag{6}$$

where  $I_0$  and I are the intensities of luminescence in the absence and presence of 1,  $K_S = k_q \tau_0$  is the Stern-Volmer constant,  $k_q$  is the bimolecular rate constant of quenching, and  $\tau_0$  is the lifetime of Ce<sup>3+\*</sup> in the absence of a quencher.

It can be seen from the results presented in Fig. 4 and Table 2 that the efficiency of quenching decreases slightly as the temperature increases, and  $K_S$  is obtained in the linear region of the curve. The lifetime of  $Ce^*(ClO_4)_3$  in MeCN-CHCl<sub>3</sub> is equal to  $\tau_0 = 28$  ns (at 296 K), which is proportional to the change in the quantum yield of luminescence, *i.e.*, it can be written:

$$\tau_0^{\ T} = \tau_0^{296} \phi^{\ T} / \phi^{296}. \tag{7}$$

where  $\tau_0^T$ ,  $\phi^T$ ,  $\tau_0^{296}$ , and  $\phi^{296}$  are the lifetimes and the quantum yields of luminescence of Ce<sup>3+\*</sup> at the given temperature and at 296 K, respectively.

The  $\tau_0$  values at different temperatures and  $k_q$  (see Table 2), which are lower than the diffusion constants at these temperatures, were calculated from Eq. (7):  $k_{\text{diff}} = 8RT/3000\eta = 1.3 \cdot 10^{10}$  (296 K) and  $1.8 \cdot 10^{10}$  (335 K) L mol<sup>-1</sup> s<sup>-1</sup>.

The positive deviation from the linear dependence in Fig. 4 can be related, first, to a static component in the quenching process, *i.e.*, to the formation of a nonluminescent  $Ce^{3+} \cdot 1$  complex in the ground state and, second, at high degrees of quenching and great



Fig. 4. Quenching of  $Ce^{*}(ClO_4)_3$  by dioxetane 1 in Stern-Volmer coordinates at 295 (1) and 335 K (2).



concentrations of the quencher, to a "seeming" static component. In the latter case, the molecules of quencher 1 are adjacent to  $Ce^{3+*}$ , *i.e.*, 1 is present in the "quenching sphere" inside which the probability of quenching is equal to unity. In this case, the modified Stern-Volmer equation has the following form:<sup>13</sup>

$$I_0/I = (1 + k_0 \tau_0[1]) \exp([1] \cdot V \cdot N/1000), \tag{8}$$

where V is the volume of the "quenching sphere" and N is Avogadro's number.

The radius of the quenching sphere was estimated from Eq. (8) using the data in Fig. 4. It turned out to be equal to 11 Å, which is greater than the sum of the radii of  $Ce^{3+}$  and 1.

Steady-state photolysis of a solution of Ce(ClO<sub>4</sub>)<sub>3</sub> in the presence of 1. Unlike other lanthanides, the quenching of Ce<sup>3+\*</sup> by dioxetane *via* an electron transfer mechanism should be the main process. When the cerium ion is excited, it becomes a strongly reducing species, since the oxidation potential  $E(Ce^{11}/Ce^{1V}) = 1.4$  V decreases by the value of the excitation energy:<sup>14</sup>

$$E^{0}(Ce^{III}*/Ce^{IV}) = E^{0}(Ce^{III}/Ce^{IV}) - E^{*} = -2.6 V.$$
 (9)

Thus, the transformations of  $Ce^{3+*}$  in the presence of 1 can be presented as Scheme 5 ( $k_{el}$  is the electron transfer rate constant and  $k_{en}$  is the energy transfer rate constant).

It follows from Scheme 5 that

$$k_{q} = \frac{(k_{ch} + k_{f})k_{daff}}{k_{ch} + k_{-1} + k_{f}},$$
 (10)

where  $k_q$  is the bimolecular rate constant of quenching of Ce<sup>3+\*</sup> by dioxetane,  $k_{ch}$  is the rate constant of the chemical reaction of Ce<sup>3+\*</sup> with 1, L mol<sup>-1</sup> s<sup>-1</sup>,  $k_{ch} = k_{cl} + k_{en}$ .

Under the condition that  $k_{el} >> k_{en}$ ,  $k_{ch}$  is determined only by  $k_{el}$ . The rate constant of the chemical reaction of  $Ce^{3+*}$  with 1 was obtained from the data on the kinetics of the consumption of 1 during steady-state photolysis.

The quantum yield of the reaction of  $Ce^{3+*}$  with 1 is the ratio of the rate of the deactivation of  $Ce^{3+*}$  resulting in the decomposition of 1 to the sum of the rates of its deactivation:

$$\mathcal{D} = -\frac{d[\mathbf{I}]}{Idt} = \frac{k_{ch}[\mathbf{I}]}{k_{d} + k_{q}[\mathbf{I}]} \,. \tag{11}$$

One can obtain from Eq. (11):

$$\frac{1}{\phi} = \frac{k_{\rm d}}{k_{\rm ch}[1]} + \frac{k_{\rm q}}{k_{\rm ch}}.$$
 (12)

For the kinetics of the decomposition of 1, we have

$$\frac{k_{\rm d}}{k_{\rm q}} \ln \frac{[\mathbf{l}]_{\rm 0}}{[\mathbf{l}]_{\rm f}} + \left( [\mathbf{1}]_{\rm 0} - [\mathbf{1}]_{\rm f} \right) = \frac{k_{\rm ch}}{k_{\rm q}} I \cdot t \,. \tag{13}$$

where  $[1]_0$  and  $[1]_1$  are the initial and current concentrations of dioxetane.

The kinetics of the consumption of 1 at different initial concentrations and the linear anamorphosis of Eq. (13) are presented in Fig. 5. It was determined from the tangent of the slope of the straight line that  $k_{ch} = (2.6\pm0.3) \cdot 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ .

The values of the quantum yields of the photocatalytic decomposition of 1 were determined from the equation

$$\boldsymbol{\Phi} = \frac{\Delta[\mathbf{I}]}{\Delta[I \cdot I]}.$$
(14)

It was obtained that  $\Phi(\pm 0.05) = 0.43$ ; 0.68; and 0.83 at [1] = 0.01; 0.03; and 0.06 mol L<sup>-1</sup>, respectively. The maximum quantum yield was determined from the data



Fig. 5. Kinetics of consumption of 1 during photolysis in MeCN-CHCl<sub>2</sub> at [1] = 0.01 (1), 0.03 (2), and 0.06 (3) mol L<sup>-1</sup> ([Ce<sup>3+</sup>] = 0.01 mol L<sup>-1</sup>, T = 293 K); kinetics of decomposition of 1 in coordinates of Eq. (13) (4):

$$y = \frac{k_{\rm d}}{k_{\rm q}} \ln \frac{[1]_0}{[1]_t} + ([1]_0 - [1]_t)$$



Fig. 6. Dependence of the quantum yield of photodecomposition of 1 on its concentration,  $[Ce^{3+}] = 0.01 \text{ mol } L^{-1}$ .

presented in Fig. 6:  $\phi_{\rm m} = k_{\rm ch}/(k_{\rm ch} + k_{\rm f}) = 1$ . This value indicates that there is no physical quenching in the  ${\rm Ce}^{3+*} \cdot 1$  complex  $(k_{\rm f} = 0)$ .

A comparison of the rate constants of the bimolecular quenching  $(k_q)$  and the chemical reaction of  $Ce^{3+*}$ with 1  $(k_{ch})$  indicates that they are almost equal within the experimental error, *i.e.*,  $k_{ch} = k_q$ . Taking into account that  $k_f = 0$ , we obtain from Eq. (9):

$$\frac{k_{\rm diff}}{k_{\rm -l}} = K^{\bullet} = 1 + \frac{k_{\rm ch}}{k_{\rm -l}} \,. \tag{15}$$

where  $K^*$  is the stability constant of the Ce<sup>3+\*</sup> · 1 complex, L mol<sup>-1</sup>.

The exponential law of the decay of the luminescence of  $Ce^{3+*}$  in the presence of 1 suggests that the equilibrium of complex forms of the lanthanide is established over a time that is shorter than the lifetime of  $Ce^{3+*}$ , *i.e.*,  $k_d > k_{-1}$ . Thus, the upper boundary  $K^* <$ 200 L mol<sup>-1</sup> at 296 K.

The values of  $E_a = 3.2\pm0.3$  kcal mol<sup>-1</sup> and logA = 11.6±0.6 were obtained from the Arrhenius dependence of  $k_q$ . This agrees with the activation parameters for the temperature dependences of the rate constants of the photoinduced electron transfer.<sup>15</sup> The results obtained confirm the assumption that in the reaction of Ce<sup>3+\*</sup> with 1 the electron transfer occurs inside the coordination sphere of Ce<sup>3+\*</sup> (Scheme 6).

The transfer of an electron to the antibonding orbital of the O-O bond of dioxetane causes dioxetane to become dissociative and to cleave rapidly to give molecule of ketone 2 and the radical anion of ketone.<sup>16</sup> The latter is localized near Ce<sup>4+</sup>, and reverse electron transfer followed by the formation of Ce<sup>3+</sup> is preferred. In

# Scheme 6

$$[Ce^{3+*} \cdot nS] + 1 \longrightarrow [Ce^{3+*} \cdot 1 \cdot nS] + (n - m)S \longrightarrow [Ce^{4+} \cdot 1^{-*} \cdot mS] \longrightarrow [Ce^{4+} \cdot 2^{-}, 2 \cdot mS] \longrightarrow [Ce^{3+} \cdot 2, 2 \cdot mS] \longrightarrow [Ce^{3+*} \cdot nS] + 2 2$$

outer-sphere electron transfer, the radical anion of ketone and Ce<sup>4+</sup> are rather remote. In this case, the interaction of the radical anion with 1 accompanied by the transfer of an electron to the dioxetane molecule is possible. As a result, the limiting quantum yield of the decomposition of 1 would be >1, which contradicts the experimental data.

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